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Treatment of Organic Dye Solutions by Electrodialysis

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ABSTRACT

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Laboratory tests were performed to determine the efficiency of dye solution desalination by electrodialysis. The study involved anionic dye and mineral salt recovery by obtaining two streams from a salt and dye mixture – dye-rich solution and salt solution. A standard anion-exchange and cation-exchange membranes or monovalent selective anion-exchange membranes were used in the ED stack. It was found that the separation efficiency was strongly dependent on the dye molecular weight. The best results for standard ion-exchange membranes were achieved for the desalination of Direct Black solution. Furthermore, the obtained results implied that the application of monovalent selective anion-exchange membranes improved the recovery of dye and salt solutions – the dye concentration in the diluate remained constant irrespective of the molecular weight of anionic dyes, whereas the salt recovery remained very high (99.5%).

1. INTRODUCTION

The textile industry produces huge amounts of waste waters heavily charged with unfixed dyes and other chemicals (salts, acids, hydroxides, dispersing and complexing agents, etc.). Purification of these complex effluents is therefore highly advisable, in view of the decrease of waste water volume, as well as the reuse of valuable substances. Among membrane processes, the electrodialysis seems to be very viable technology for the desalination of solutions containing organic substances.

Electrodialysis (ED) has been developed and applied for desalination and concentration of salty waters and industrial effluents since the 1950s (Baker 2000). Desalting of brackish waters and the production of boiler feed water and industrial process water are the main ED applications. And what is more, electrodialysis is one of the technologies that offer an opportunity to separate charged components from neutral substances. Fractionation of mono- and multi-valence ions of the same sign is also possible with the use of electro-membrane processes.

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(1) Professor

Electrodialysis is now a technology which has been widely used in chemical, food and pharmaceutical industry (Tu 2005). The important ED applications involve: recovery of mineral and organic acids, milk whey desalination, desalination of protein products, glutamine and amino acids, production of vitamin C and lactic acid (Nagarale 2006). On the other hand, there are only a few references dealing with direct application of electrodialysis in the treatment of salty industrial effluents. A waste water reclamation and reuse plant (Taiwan) established to treat effluents from steel production demonstrated the technical and economical feasibility of electrodialysis reversal (EDR) process (Chao 2008). A hybrid microfiltration (MF) and electrodialysis (ED) system was successfully employed to remove the color and contaminants of paper industry waste water. Chandramowleeswaran et al. (Chandramowleeswaran 2006) proved that electrodialysis was also a promising technology for the treatment of textile effluents for TDS reduction to reuse the received water for production cycle.

Organic compounds are often very valuable fraction in waste waters. Some organic substances are non-charged and their separation from ionic constituents by ED seems to be rather easy. Singlande et al. (Singlande 2006) found that acetic acid as a neutral compound was retain in the course of ED process under the presence of mineral salt (NaCl and Na_2SO_4). The true difficulties arise when charged organics should be separated because they can migrate under the electric field conditions. Zhang et al. (Zhang 2009) investigated separation of various organic compounds (acetate, glycine, aspartate, protonated lysine, methyl ammonium ion) in the ED process applying standard ion-exchange membranes and monoselective ion-exchange membranes. They concluded that the size effect took an important role in the separation of organic ions by ED.

The study aimed at the evaluation of the usability of electrodialysis process in the desalination of organic dye solutions. It was anticipated that by applying ion-exchange membranes and the electric field, separation of dye macroparticles from mineral salts will be possible. Although, organic dyes can dissociate in water solution, but taking into consideration the size of dye particles (1-10 nm), it does not seem probable that dyes will migrate through ion-exchange membranes.

The reported investigation are the continuation of the previous study (Majewska-Nowak 2010). The idea of the treatment of dye effluents from dye-house involves recovery of valuable substances (dyes, salts) and water reuse, and the integrated ultrafiltration-electrodialysis system was proposed (Fig. 1). Thus, the feed model solutions contain small dye amounts, characteristics of UF permeates.

2. MATERIALS AND METHODS

2.1. Membranes and electrodialysis equipment

The study on the desalination of dye-salt mixtures was performed with use of a lab-scale electrodialysis apparatus. Standard PC-SK cation-exchange and PC-SA anion-exchange membranes (PCA GmbH, Germany) were used in the preliminary tests (Table 1). Standard CMV Selemion (Asahi Glass, Japan) cation-exchange and monovalent selective ACS Neosepta (Tokuyama Soda, Japan) anion-exchange membranes were chosen for basic experiments (Table 2). Each membrane had an effective area of 64 cm².

Table 1. Properties of the ion-exchange membranes applied in the preliminary experiments

Parameter	Membrane	
	Cation-exchange PC-SK	Anion-exchange PC-SA
Producer	PCA GmbH (Germany)	
Thickness, µm	90-130	
Ion-exchange capacity, mmol/g	approx. 1.2	approx. 1.1
Electrical resistance, Ω cm^2	1-3	1-3
Thermal stability, °C	Maximal 60	Maximal 60
Chemical stability (pH range)	0-9	0-9
Burst strength , MPa	0.4	0.5
Permselectivity (transfer number) t-K$^+$ t-Cl$^-$	>0.95	>0.93
Ionic form	Na$^+$	Cl$^-$
Functional group	-SO$_3^-$	-NR$_4^+$

Table 2. Properties of the ion-exchange membranes applied in the basic experiments

Parameter	Membrane	
	Cation-exchange CMV Selemion[1]	Anion-exchange ACS Neosepta[2]
Producer	Asahi Glass Corp. (Japan)	Tokuyama Soda Corp. (Japan)
Thickness, µm	130-150	150-200
Ion-exchange capacity, mmol/g	approx. 2.4	1.4-2.0
Electrical resistance, Ω cm^2	2.0 – 3.5 (0.5 M NaCl)	2-2.5 (0.5 M NaCl)
Thermal stability, °C	Maximal 40	High
Chemical stability	high	high
Burst strength , MPa	0.16	0.15
Permselectivity (transfer number) t-Na$^+$ t-Cl$^-$	>0.96	>0.98
Permselectivity (transfer number) of multivalence anions (SO$_4^{2-}$)	-	< 0.005
Ionic form	Na$^+$	Cl$^-$
Functional group	-SO$_3^-$	-NR$_4^+$

[1] data available at http://www.agec.co.jp

[2] data available at http://www.astom-corp.jp

There were 10 cell pairs in the ED stack. Each cell pair contained a diluate and a concentrate compartment, thus 10 anion-exchange and 11 cation-exchange membranes were arranged in the stack (PCCell 64002 model). The ED stack operated as an integral part of the installation PCCell BED-1 produced by PCCell GmbH, Germany (Fig. 2, Table 3) (PCCell ED 64002 manual, 2010).

Table 3. Characteristics of two-chamber electrodialysis stack PCCell 64002

Membrane size , cm	11 x 11
Effective membrane area, cm^2	64
Cell thickness, mm	0.5
Number of cell pairs	Up to 20
Anode	Platinum coated titanium
Cathode	Steel V4A
Electrode housing	Polypropylene

2.2. Experimental and analytical methods

The electrodialysis desalination process was carried out for water salt solution and model salt solution containing various organic dyes (Merck, Zachem) (Table 4). The applied dyes were of an anionic type and varied in molecular weight. Dye concentration in the feed (diluate) solutions amounted to 8-12 mg/L. This range of concentration was characteristics of UF permeates after dye solution decolorization. Sodium chloride (NaCl) was used as a mineral salt in water solutions and dye aqueous mixtures. Salt concentration in the feed (diluate) water solutions was equal to 1, 2, 5, and 10 g NaCl/L, whereas for ED experiments with organic dyes, the dye mixtures containing 1 g NaCl/L were used.

In the course of ED experiments, the volume of diluate and concentrate was equal to 2 L. As initial concentrate and diluate, the same salt solution was used. However, the organic dyes were added only to diluate feed solutions. 0.1 N H_2SO_4 solution was used as a electrode rinsing solution.

The ED desalination experiments were performed at a constant electrical current and the applied current density was equal to 3.12, 6.24, 15.6, and 31.2 mA/cm^2 (salt water solutions) and to 1.56 mA/cm^2 (dye-salt mixtuers) The ED system operated in a batch mode, i.e. both diluate and concentrate circulated in the stack till the end of desalination process. The process was stopped when the maximum voltage had been achieved (24.5 V). Further continuation of the desalination brought the decrease in the applied current.

During the ED process diluate and concentrate samples were collected every 5-10 minutes. The variation in voltage was also monitored. The concentration of organic dyes in both diluate and concentrate were determined spectrophotometrically at the wavelengths given in Table 4, which correspond to the maximum absorbance of the sample. A spectrophotometer UVMINI-1240 (Shimadzu) was used to determine dye solution absorbance.

Salt concentration in diluate and concentrate was determined indirectly by measuring the solution conductivity (with the use of conductivity meter Elmetron CC-411).

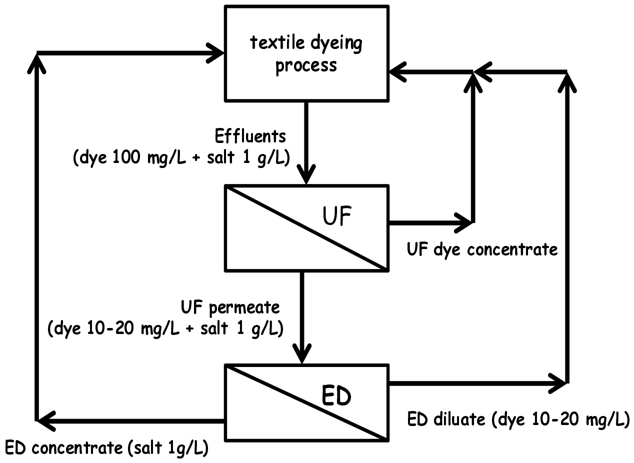

Fig.1. The idea of dye effluent treatment by integrated UF-ED system

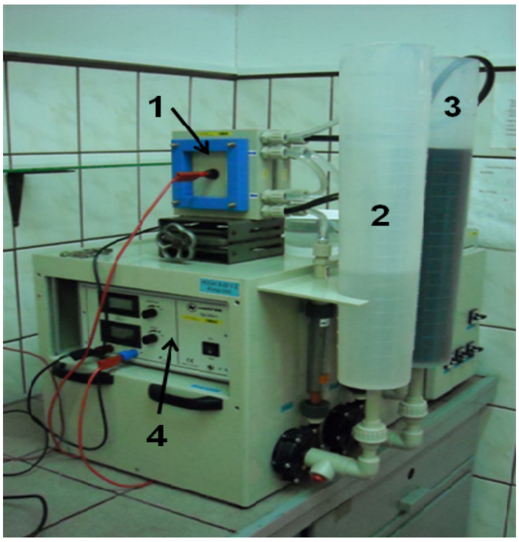

Fig. 2. Electrodialysis installation PCCell:
1 – electrodialysis stack, 2- concentrate tank, 3 – diluate tank, 4 – power supply

Electrical energy consumption (EC) in the ED desalination of dye-salt mixtures was calculated using the Eq.(1):

$$EC = \frac{I\int_0^t U dt}{V_d} \tag{1}$$

where:
EC – electrical energy demand per 1 m^3 of treated solution, kWh/m^3
I - current intensity, A
U – voltage, V
V_d – volume of the diluate, m^3
t – time of the process, s

Table 4. Characteristics of the experimental dyes

Dye	Molecular weight, Da	Classification	pH[1]	Dye symbol	λ_{max} ,[2] nm	Structural formula
Methyl Orange C.I.[3]13025	327	Acid dye	5.7	MO	465	$C_{14}H_{14}N_9O_9SNa$
Indigo Carmine C.I. 73015	466	Acid dye	5.5	IC	610	$C_{16}H_8N_2Na_2O_8S_2$
Amido Black C.I. 20470	615	Acid dye	5.7	AB	618	$C_{22}H_{14}N_6Na_2O_9S_2$
Titan Yellow C.I 19540	696	Direct dye	5.5	TY	399	$C_{28}H_{19}N_5Na_2O_6S_4$
Direct Green C.I. 30315	878	Direct dye	6.1	DG	370	$C_{35}H_{21}N_8Na_3O_{12}S_2$
Direct Blue C.I. 34140	1029	Direct dye	7.2	HB	577	$C_{40}H_{23}N_7Na_4O_{13}S_4$
Direct Black C.I. 35435	1084	Direct dye	7.6	DB	585	$C_{44}H_{32}N_{13}O_{11}S_3Na_3$

[1] Determined for the dye solutions of concentration equal to 100 mg/L
[2] Wavelength corresponding to the maximum absorbance of the dye solution
[3] Colour Index number

3. RESULTS AND DISCUSSION

3.1. Preliminary tests on saline water desalination with the use of standard ion-exchange membranes

The aim of these preliminary tests was to evaluate the ED desalination process with the use of standard PCA membranes, as well as to verify the operation conditions of the PCCell BED-1 installation. The operational parameters, i.e. the applied electrical current has been chosen in a such way to not exceed the limiting current density. The limiting current density was evaluated theoretically on the basis of Rautenbach et al. (Rautenbach 1989) approach with assumption that the final salt concentration in the diluate cells should not exceed 5-10% of the initial salt concentration.

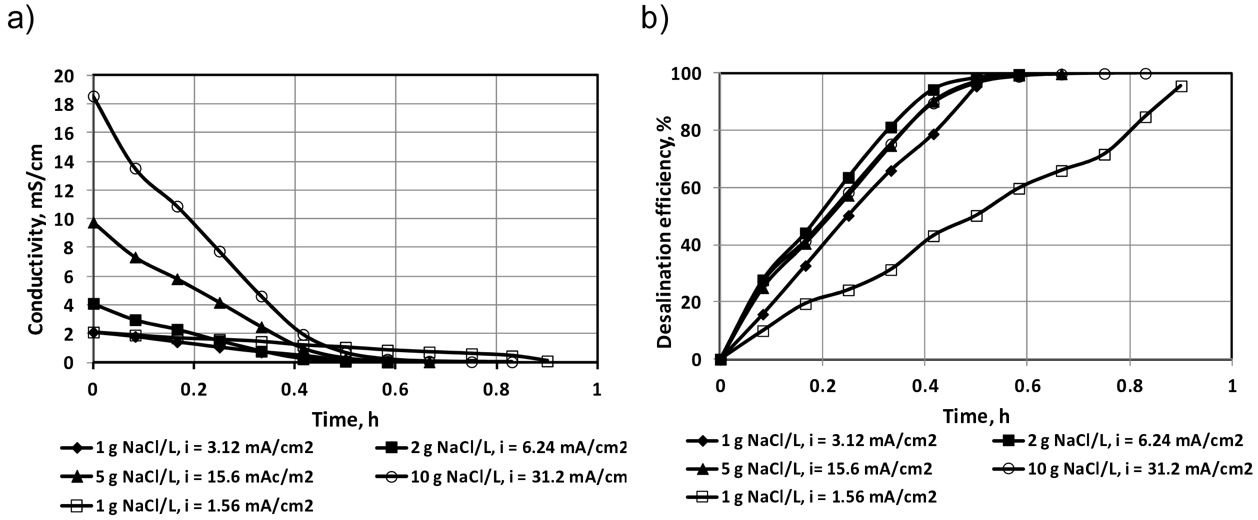

Fig. 3. Desalination of NaCl solutions by electrodialysis: a) diluate conductivity versus operation time, b) desalination efficiency versus operation for various salt content.

The effect of salt content in the treated solution on ED efficiency is shown in the Fig.3. The obtained desalination efficiency at a constant current density was rather high (90-95.5%), irrespectively of the initial salt concentration. However, the final diluate concentrations varied in a great extend and amounted to 96; 239; 971 and 1949 µS/cm for NaCl content equal to 1, 2, 5 and 10 g/L, respectively. It was also possible to reach very low diluate conductivity (in the range of 25-45 µS/cm) for all experiments, but this brought about the decrease in the current density. The results plotted in Fig. 3 involve also data for decreasing applied current, i.e. to reach maximal desalination degree.

It was also observed that the desalination time increases with the increasing salt content, although the applied current was increased proportionally, according to the Faraday's law. This finding can be attributed to the worsening of the conditions of the ion selective migration, due to the increased concentration gradient between concentrate and diluate cell.

3.2. Desalination of dye-salt mixtures with the use of standard ion-exchange membranes

First of all, the experiments aimed at evaluating the application of electrodialysis for desalination of dye-salt solutions. The most important was to receive two streams after ED process: dye solution free of mineral salt and salt solution free of dye particles. Moreover, the dye concentration in the diluate should remain constant at the level comparable to the initial dye concentration.

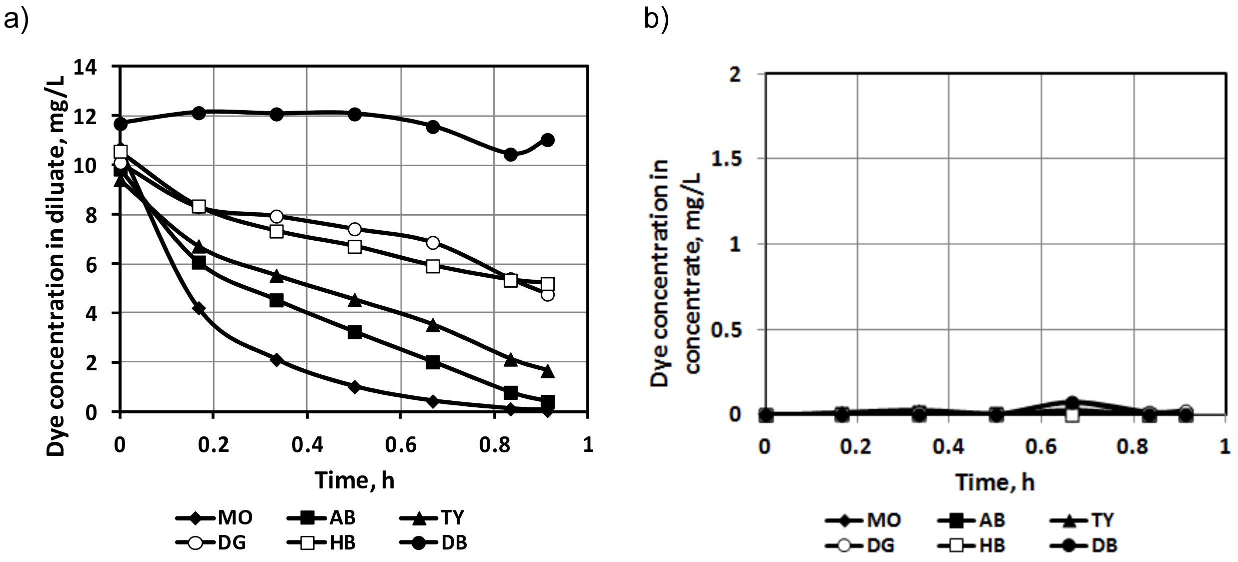

Fig. 4. Desalination of dye-salt mixtures with the use of standard ion-exchange membranes: a) dye concentration in diluate versus time of ED process, b) dye concentration in concentrate versus time of ED process for various organic anionic dyes. Current density – 1.56 mA/cm^2; initial NaCl concentration in diluate and concentrate – 1 g NaCl/L.

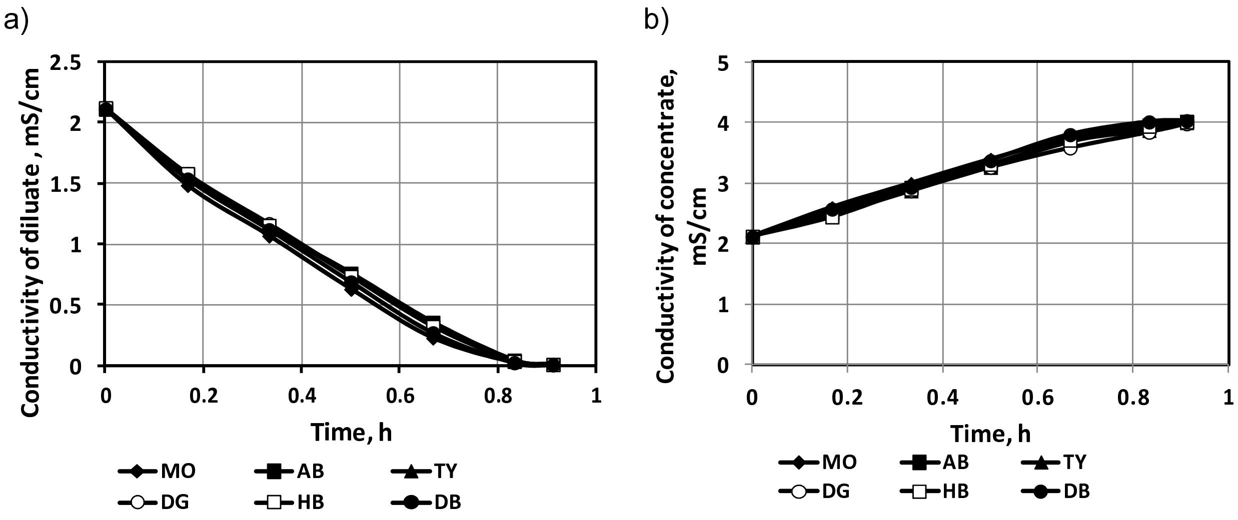

Fig. 5. Desalination of dye-salt mixtures with the use of standard ion-exchange membranes: a) diluate conductivity versus time of ED process, b) concentrate conductivity versus time of ED process for various organic anionic dyes. Current density – 1.56 mA/cm^2; initial NaCl concentration in diluate and concentrate – 1 g NaCl/L.

The effect of the dye molecular weight on the ED efficiency was verified. The experiments were carried out for six organic dyes of anionic type. The feed solutions contained dyes at concentrations typical of UF permeates, whereas NaCl concentration was equal to 1 g/L, both in diluate and concentrate feed solutions.

Fig. 4 gives the plots of dye concentrations in diluate and concentrate in the course of electrodialysis process with standard ion-exchange membranes. According to these plots, it can be concluded that only for one dye solution, i.e. containing Direct Black, the desalination result was satisfactory – the dye concentration in the diluate was maintained at a nearly constant level, whereas almost complete salt removal was achieved. The other experimental dyes behaved in a quite different way – the dye concentration was decreasing with increasing operation time, although there was no migration of dye particles into concentrate cells. This phenomenon was more pronounced for dyes characterized by lower molecular weights. Such behavior of anionic dyes indicates that dye particles are subjected to membrane sorption phenomenon. Although dye macro-anions are much greater in size than sodium anions, the structure of the standard PCA membranes enabled dye sorption into membrane matrix. Only when the highest-molecular-weight dye was tested, its penetration into anion-exchange membrane was impossible. It can be concluded that the size effect took an important role in the separation of various organic dyes from mineral salt by electrodialysis with standard ion-exchange membranes.

Taking into consideration the mineral salt migration through standard ion-exchange membranes, it can be stated that this process was getting on with no difficulty. It should be pointed out that the desalination kinetics followed almost the same pattern, irrespectively of the dye used (Fig. 5).

3.3. Desalination of dye-salt mixtures with the use of standard cation-exchange membranes and monovalent selective anion-exchange membranes

Taking into consideration the main goal of the experiments, i.e. receiving of the two valuable streams (dye solution and salt solution) from a waste effluent, the further step of the study involved application of monovalent selective anion exchange membranes instead of a standard type. The use of standard ion-exchange membranes gave satisfactory results only in case of one dye – Direct Black (Fig. 4). It was anticipated that replacement of anion-exchange membranes by mono-anion-exchange membranes would hinder the migration of dye macro-anions into anion-exchange membranes.

The results of ED desalination of salt solutions containing various anionic dyes are shown in Figs. 6 and 7. The plotted relationships revealed that it was possible to keep the dye concentration in the diluate at a constant value, irrespectively of the dye molecular weight. The implemented mono-selective anion-exchange membranes were a sufficient barrier to stop the migration of dye macro-anion into the membranes. This phenomenon can be explained on the basis of size exclusion. Probably, the ACS membranes are more dense than PC-SA membranes, thus both the diffusion and the electrical transport are influenced by smaller pores of the ACS membranes. On the other hand, the transport of small mineral ions (Na^+ and Cl^-) occurred with no obstruction. However, after 50 minutes of operation the electrical conductivity of the diluate received with ACS membranes was slightly higher than the electrical conductivity of the dilutate obtained with PC-SA membranes (approximately 100 µS/cm and 40 µS/cm, respectively) (Figs. 5 and 7). This can be explained by the fact that the electrical resistance of the ACS membranes is higher than the resistance of PC-SA membranes (Table 1 and 2). Thus, the limiting voltage drop (24.5 V) was reached earlier when the ACS membranes were used.

The applied membrane combination enabled complete separation of dye particles from mineral salt.

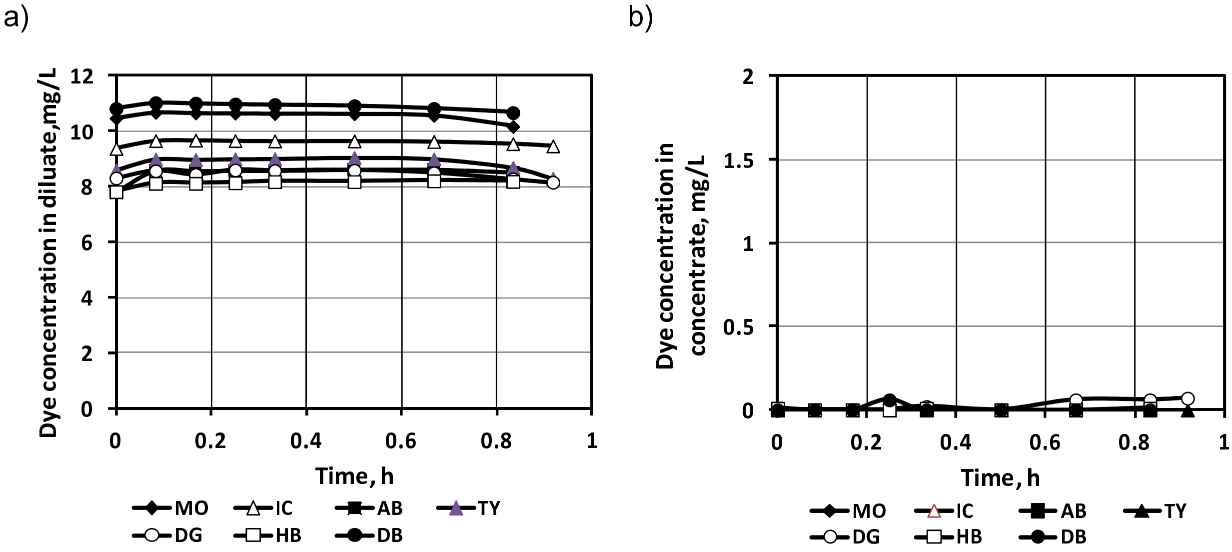

Fig. 6. Desalination of dye-salt mixtures with the use of standard cation-exchange membranes and monoselective anion-exchange membranes: a) dye concentration in diluate versus time of ED process, b) dye concentration in concentrate versus time of ED process for various organic anionic dyes. Current density – 1.56 mA/cm^2; initial NaCl concentration in diluate and concentrate – 1 g NaCl/L.

The electrical energy consumption (EC) in the course of the electrodialysis of dye-salt solutions was calculated (Table 4). From the results obtained in can be inferred that the power consumption is almost of the same value for all tested solutions, including aqueous salt solution (with no dye addition). This finding is quite obvious in the view of Faraday's law. However, a slight shift towards higher power demand was observed with the increasing of dye molecular weight. This can be probably attributed to the hampered ion transport in the presence of large dye macro-anions and increasing cell resistance. Nevertheless, the calculated power consumption is very sensible. It should be noted that the data given in Table 4 do not involve energy demand for pumping of circulated solutions in the ED installation.

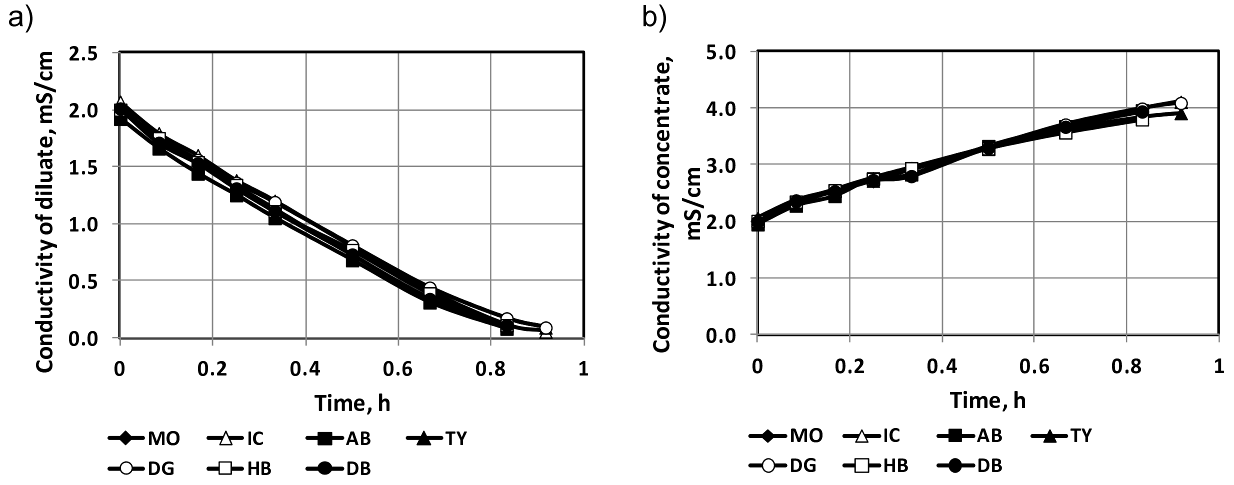

Fig. 7. Desalination of dye-salt mixtures with the use of of standard cation-exchange membranes and monoselective anion-exchange membranes: a) diluate conductivity versus time of ED process, b) concentrate conductivity versus time of ED process for various organic anionic dyes. Current density – 1.56 mA/cm^2; initial NaCl concentration in diluate and concentrate – 1 g NaCl/L.

Table. 4. Energy consumption (EC) for ED desalination of dye-salt mixtures (salt 1 g NaCl/L, i = 1.56 mA/cm^2)

Dye Parameter	MO	IC	AB	TY	DG	HB	DB	H_2O
EC (kWh/m^3)	0.38	0.40	0.49	0.55	0.48	0.48	0.49	0.47

CONCLUSIONS

1. The electrodialysis process with standard ion-exchange membranes enabled efficient desalination of organic dye solutions only for high-molecular-weight dye (Direct Black). The concentration of low-molecular-weight dyes in the diluate decreased with operation time, which was attributed to the sorption of dye particles in the membrane structure.
2. The size effect took an important role in the separation of various organic dyes from mineral salt by electrodialysis with standard ion-exchange membranes.
3. The electrodialysis with standard cation-exchange and monovalent selective anion-exchange membranes allowed satisfactory desalination of anionic dye solution, irrespectively of the dye type. Two streams from a salt and dye mixtures were received – one being enriched with dye alone (diluate), and the other one being a salt solution with no organic matter (concentrate).

ACKNOWLEDGEMENTS

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